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Orientation relationship between metallic thin films and quasicrystalline substrates.

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ABSTRACT
We present experimental results on the structure of Ag thin films grown on high-symmetry surfaces of both quasicrystals and approximants. For coverages above ten monolayers, Ag form *fcc* nanocrystals with (111) plane parallel to the surface plane. Depending on the substrate surface symmetry, the Ag nanocrystals exist in one, two or five different orientations, rotated by a multiple of $2\pi/30$. The orientation relationship between crystalline films and substrates appears to be determined by the following principles : high atomic density rows of the adsorbate are aligned along high atomic density rows of the substrate.

INTRODUCTION

The orientation relationship between crystalline thin films and quasicrystalline substrates has been investigated in two different situations. In a first case, the crystalline overlayer is artificially produced by sputtering and annealing the surface [1]. Variations of the sputtering yield across the different elemental constituents result in a shift of the composition from the quasicrystalline phase to a cubic phase with CsCl structure. If the annealing temperature is sufficiently low, the quasicrystalline structure is not recovered and the cubic phase can be observed experimentally as an overlayer. In the second situation, the thin crystalline film is formed by adsorption of extrinsic atoms from the vapor phase through nucleation and growth. This has been realized for a number of systems, where a metal (like Al, Ag, Au or Cu) was deposited onto a high symmetry surface of an icosahedral (AlPdMn or AlCuFe) or decagonal (AlNiCo) substrate [2-4]. When the film becomes thick enough, it usually recovers its crystalline structure, with specific orientation relationship relative to the substrate. Here we present our results for Ag thin films deposited on the 2-fold and 5-fold surfaces of the icosahedral AlPdMn QC, the pseudo-10-fold surface of the ξ'-AlPdMn orthorhombic approximant and the 10-fold surface of the AlNiCo decagonal QC. The orientation relationship between crystalline films and substrates are interpreted using arguments based on alignment of high atomic density rows within the interface plane rather than alignment of symmetry axes.

EXPERIMENTAL DESCRIPTION

Single grains from the $Al_{72}Pd_{19.5}Mn_{8.5}$ icosahedral quasicrystalline (IQC) phase and from the ξ'-$Al_{77.5}Pd_{19}Mn_{3.5}$ approximant were grown by the Bridgman method. The $Al_{72}Ni_{11}Co_{17}$ decagonal quasicrystalline (DQC) sample were grown by a flux method (slow cooling). High symmetry surfaces were extracted from the single grains after orientation within ±0.2° by back-Laue scattering and polished down to a final roughness of 0.25 μm, which leads to a mirror like aspect. Clean and well ordered surfaces were obtained in ultra-high vacuum (UHV) by repeated cycles of sputtering (Ar^+, 2 to 0.5 kV) and annealing (up to 820 K, 900 K and 970 K for ξ', IQC and DQC respectively). Silver is deposited using an electron-beam evaporator, with the substrate held at

room temperature and a background pressure better than 2.10^{-10} torr. The UHV chamber is equipped with a LEED-Auger spectrometer and an Omicron scanning tunneling microscope. More details can be found in reference [3].

RESULTS

Figure 1 shows three 250x250 nm^2 STM images of a relatively thick Ag film deposited on the 2-fold (Fig. 1a) and 5-fold (Fig. 1b) surfaces of the $Al_{72}Pd_{19.5}Mn_{8.5}$ icosahedral quasicrystal and the pseudo-10-fold surface of the ξ'-$Al_{77.5}Pd_{19}Mn_{3.5}$ approximant (Fig. 1c). The thickness of the films is larger than 10 monolayers (ML) in every case. These images show the formation of Ag pyramid-like nanocrystals with hexagonal shape. It looks very much like Ag deposited on Ag(111) surface, where growth involves kinetic roughening leading to the formation of wedding-cake structures [5]. Vertical growth of the Ag film, instead of layer-by-layer growth, occurs as a consequence of limited interlayer transport of Ag adatoms within our experimental conditions of deposition flux, temperature and pressure. The hexagonal shape of the nanocrystals suggests that the Ag films have adopted the *fcc* symmetry with the (111) axis parallel to the surface normal. This is confirmed by STM images with atomic resolution recorded on top of one these nanocrystals that shows an hexagonal 2D lattice.

In Fig.1, the hexagonal nanocrystals all have the same orientation relative to the 2-fold substrate, which does not appear to be the case for the 5-fold substrate for example. Actually, by measuring carefully the angles between the edges of hexagonal islands, one can conclude that the nanocrystals display specific relative orientations on this surface. For the 5-fold IQC substrate, the angle between edges of pairs of islands always equals a multiple of 12° (0, 12, 24, 36, etc...), i.e. a multiple of $(2\pi/5 - 2\pi/6) = 2\pi/30$. In other words, the *fcc* Ag islands exist in five different orientations, rotated by 36° and forming a 5-fold symmetrical arrangement. For the p-10f surface of the ξ' approximant, the angles between step edges of pairs of islands are always equal to either 0 or 12° and the *fcc* islands therefore exist in two different orientations relative to the substrate, rotated by $2\pi/30$. Grain boundaries can be observed within a single layer separating two Ag nanocrystalline domains rotated by $2\pi/30$. As mentioned above, *fcc* islands exist in only one orientation on the 2-fold IQC substrate.

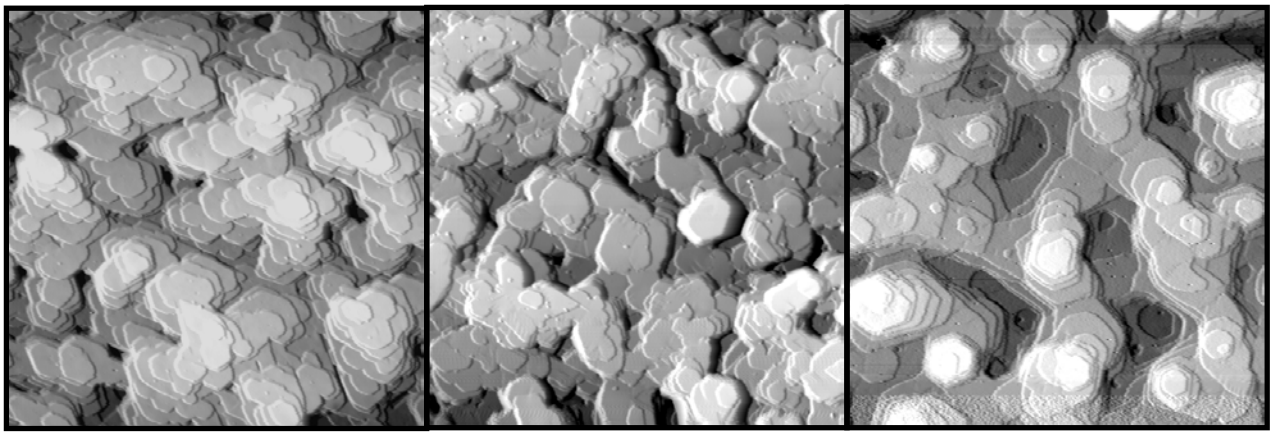

Figure 1 : STM images (250x250 nm^2) of Ag thin films (θ>10 ML) deposited on the 2-fold (left) and 5-fold (center) surfaces of the $Al_{72}Pd_{19.5}Mn_{8.5}$ icosahedral quasicrystal and the pseudo-10-fold surface of the ξ'-$Al_{77.5}Pd_{19}Mn_{3.5}$ approximant (right).

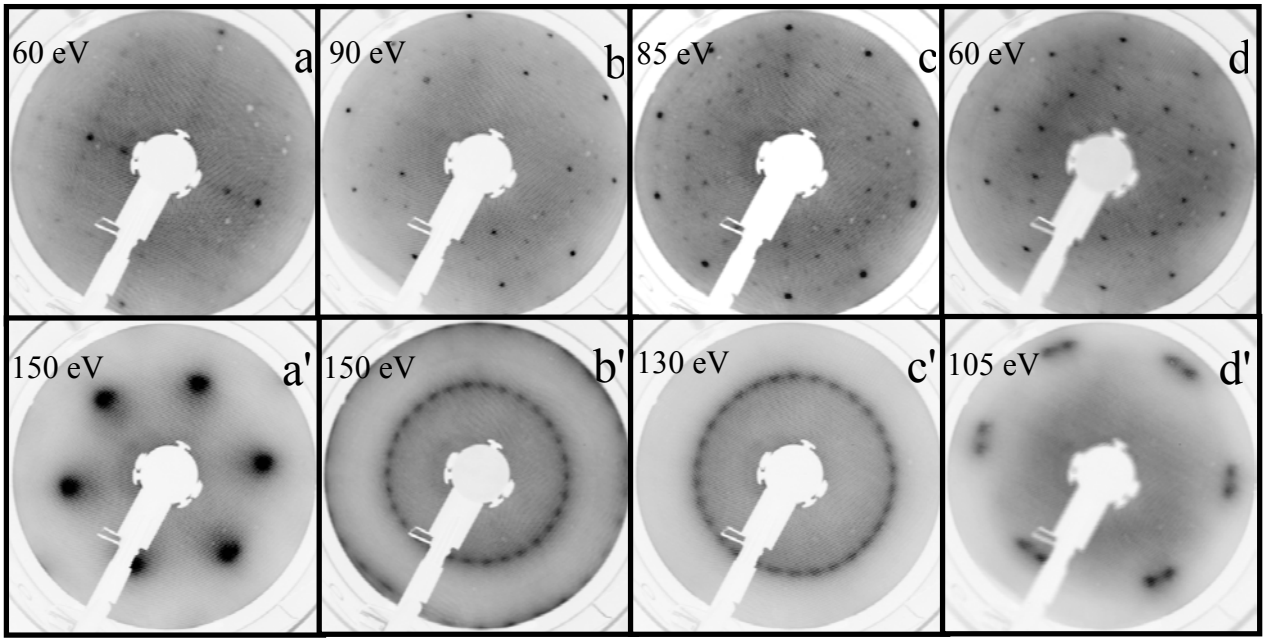

Figure 2 : LEED patterns of the 2-fold IQC (a, a'), 5-fold IQC (b, b'), 10-fold DQC (c, c') and pseudo-10-fold surface of the ξ' approximant (d, d'). Top row : clean surfaces. Bottom rows : surfaces dosed with >10 ML of Ag. Energy of the incident electron beam is specified for each diffraction pattern.

The LEED patterns, including that of the 10-fold surface of the AlNiCo DQC, are shown in Fig. 2 both before and after Ag deposition. The thickness probed by LEED is less than 10 ML and therefore the diffraction patterns shown in the bottom row of Fig. 2 give information on the atomic structure of the Ag films only. Each of the diffraction patterns recorded after Ag deposition is based on a hexagonal pattern, confirming the [111] orientation of the *fcc* Ag nanocrystals. In all four cases, the diffraction spots converge toward the specular (00) reflection, hidden by the shadow of the electron gun, when the energy of the primary-electron beam is varied. Therefore the [111] axis of Ag nanocrystallites is always parallel to the symmetry axis of the substrate along the surface normal. This was expected as the top of the Ag islands does not appear to be tilted with respect to the surface plane in our STM images.
For the 2-fold substrate, the diffraction pattern of the Ag film is made of only one hexagonal pattern, in agreement with our STM data suggesting that Ag nanocrystals all have the same orientation relationship with respect to the substrate. The diffraction pattern of the Ag film deposited on the 5-fold surface appears as a ring containing 30 spots resulting from the 5-fold twinning of the *fcc* Ag nanocrystals. The angular displacement between two adjacent hexagonal patterns is indeed equal to $2\pi/30$, in agreement with the angles measured between the step edges of pairs of islands being equal to a multiple of $2\pi/30$ in the STM images. This is also true for the 10-fold AlNiCo DQC substrate. Finally, the diffraction pattern of the Ag film deposited on the p-10f surface of the ξ' approximant is made of two hexagonal patterns with an angular displacement between them equal to about $12° \sim 2\pi/30$. This again confirms the above STM-based interpretation that the Ag *fcc* nanocrystallites are formed according to two distinct orientations relative to the substrate, rotated by about 12° around their [111] growth axis. Finally we note that the results obtained by LEED (which probes about 1 mm^2) are consistent with the nanoscaled picture provided by the STM.

DISCUSSION

We discuss below some arguments regarding the physical mechanism determining the orientation relationship between a crystalline film on top of a quasicrystalline substrate. First, it is interesting to note that twinning also occurs at crystalline interfaces. A simple situation is that of *fcc*(111)/*bcc*(110) interfaces where preferred epitaxial relationships are those in which the most densely packed rows ($[1\,\bar{1}\,0]$) in the *fcc*(111) plane are parallel to one of the densely packed rows in the *bcc*(110) plane ($[\bar{1}\,11],[1\,\bar{1}\,1],[001]$) (see Fig. 3) [6,7]. When $fcc[1\,\bar{1}\,0] \parallel bcc[001]$, then only one domain occurs and the diffraction pattern looks like that of Fig. 2a'. This is called the Nishiyama-Wasserman (NW) orientation. When $fcc[1\,\bar{1}\,0] \parallel bcc[\bar{1}\,11]$ or $bcc[1\,\bar{1}\,1]$, two equivalent domains occur rotated by ± 5.26° relative to the NW direction. This is called the Kurdjumov-Sachs orientation (KS). The hexagonal diffraction pattern then splits into two domains separated by an angle of ~10°, and the LEED pattern looks very similar to that shown in Fig. 2d'. The selection between the NW or KS orientation relationship mostly depends on the lattice parameter ratio a_{fcc}/a_{bcc}.

Let us now examine the situation for the Ag *fcc*(111)/2-fold-IQC interface. The *fcc*[111] axis is parallel to a 2-fold axis of the IQC. The situation can be illustrated by an icosahedron representing the icosahedral phase inside a cube, where a 2-fold axis of the IQC is coincident with a [111] axis. Then in the 2-fold plane, we find two 5-fold axis which are nearly coincident with $[01\,\bar{1}]$ and $[10\,\bar{1}]$ rows. The angle between these two 5-fold axes is 2.arctan(1/τ)~63°, i.e. very close to 60°. In the 2-fold plane, densest directions show up perpendicular to the 5-fold directions [8], that is along the dense $[0\,\bar{1}\,1]$ and $[\bar{1}\,01]$ rows of the cubic lattice. If the epitaxial relationship between the Ag film and the 2-fold IQC substrate is guided by the same principle, i.e. that the most densely packed rows of the adsorbate and substrate should parallel each other, then Ag islands should appear in only one orientation, in agreement with experiments. This is because the angle between the two dense directions on the 2-fold IQC surface is nearly 60°. Note that the small angular mismatch between high-density atomic rows of the substrate and adsorbate (2.arctan(1/τ)~63° instead of 60°) should produce some orientational disorder from one crystallite to the other that could explain the larger size of the diffraction spots observed in Fig. 2a' as compared to the other cases (e.g. Fig 2b').

Within the 5-fold plane of the IQC surface, the most densely packed directions are defined by a set of five 2-fold axis separated by 36°. In this case, the most densely packed rows ($[1\,\bar{1}\,0]$) in the *fcc*(111) plane cannot coincide with the dense directions of the 5-fold substrate because a 36° rotation is not commensurate with a 60° rotation. Therefore the Ag islands should occur in five different domains, rotated by 36°, again in agreement with experiments. Therefore coincidence of densely packed atomic rows common to the substrate and the adsorbate seems to be the driving force by which the memory of the substrate symmetry is mediated through thick Ag films. We have shown previously that for the 5-fold surface, the nucleation and growth of the Ag film proceeds by capture of diffusing adatoms and further aggregation. Ag islands first grow vertically and then expand laterally [3]. Alignment of the symmetry axes of the Ag islands relative to the substrate should be initiated at low coverage and it becomes apparent in the STM images only for a thicker film where pyramid-like nanocrystals are formed.

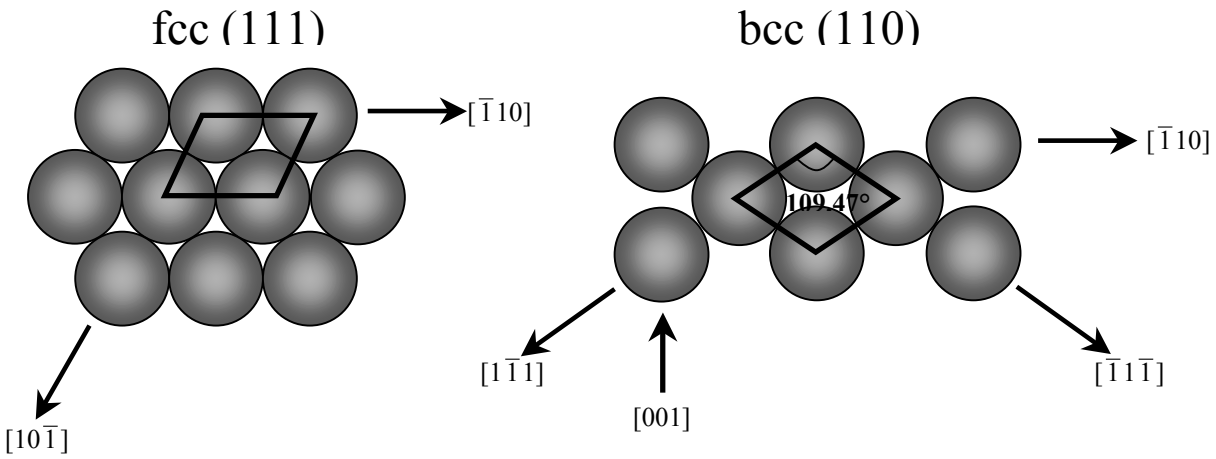

Figure 3 : Schematic description of the *fcc* (111) and *bcc* (110) planes.

In the case of the p-10f surface of the ξ' approximant, experimental results indicate that the Ag nanocrystallites are formed according to two distinct orientations relative to the substrate, rotated by ~12° around their [111] growth axis. In order to determine if the same principle prevails in determining the epitaxial relationship with the Ag film, we need to find out the directions of the most densely packed rows of atoms within the pseudo-10-fold surface plane. For this, we use the bulk structural model proposed by Boudard [9]. Figure 4 shows two examples of planes perpendicular to the pseudo-10-fold axis of the ξ' phase, which is the **b** axis of this orthorhombic approximant. In the (**a**, **c**) plane, motifs with pentagonal and decagonal symmetry can be found, located approximately at the vertices and the center of the rectangular unit cell. High atomic density rows can be found oriented along the edges of the pentagonal motifs, i.e. with (almost) 5-fold symmetry. However if the dense ([1$\bar{1}$0]) rows of Ag crystals were aligned along these lines, then we should expect the Ag islands to appear in five different orientations as for the 5-fold IQC surface, in contradiction with experiment. High density atomic rows can also be found along the [10$\bar{1}$] and [$\bar{1}$0$\bar{1}$]direction in the (**a**, **c**) plane. The angle between these two directions (noted by arrows in Fig. 4) is 108.4°, which is very close to the angle between dense directions in a *bcc* (110) plane (109.47°). If dense atomic rows of Ag *fcc* (111) plane are aligned along these dense rows of the pseudo-10-fold plane, then Ag nanocrystals should appear according to two different orientations rotated by 11.57°. This is consistent with our experimental data, considering the uncertainty in determining precisely the rotation angle between the two domains due to the width of the diffraction spots.

We mentioned earlier that the diffraction pattern shown in Fig. 2d' for the Ag(111)/ p-10f-ξ' interface looks very similar to that observed for *fcc*(111)/*bcc*(110) interfaces with the KS orientation relationship. This is actually not surprising considering the close similarity between the angle formed by high-density atomic rows in *bcc* (110) and p-10f-ξ' substrates, i.e. 109.47° and 108.4° respectively.

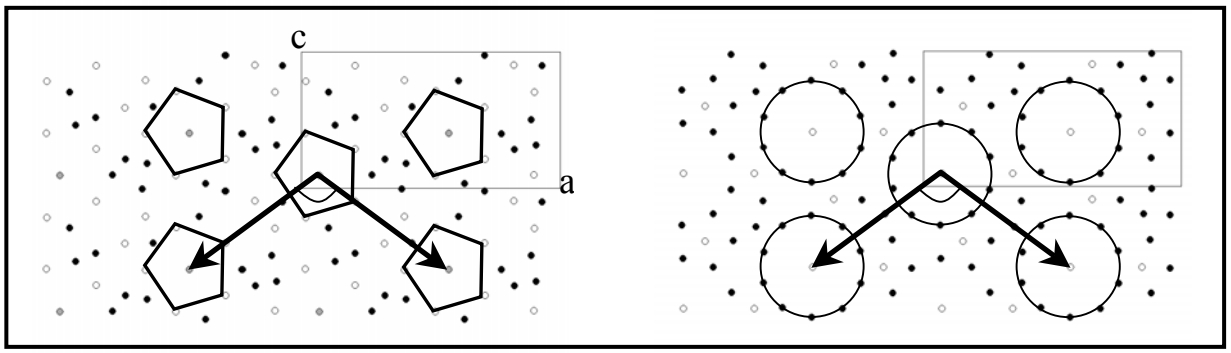

Figure 4 : Atomic layers perpendicular to the $\mathbf{b}_{\xi'}$ axis of the ξ' phase, according to the structure model by Boudard, *et al*.[9]. Angle between arrows is ~108°.

CONCLUSION

We have presented an analysis of the structure of Ag thin films grown on high-symmetry surfaces of both quasicrystals and approximants. The formation of Ag nanocrystals with *fcc* structure is observed on all substrates for coverages above ten monolayers. The dense *fcc* (111) plane is parallel to the surface plane. The nanocrystals still retains the symmetry of the substrate on which the growth started at a mesoscopic scale, as evidenced by the *n*-fold twinning of nanocrystallites, where the index *n* depends on the substrate symmetry. The orientation relationship of the nanocrystallites with respect to the substrate – and therefore the *n*-fold twinning – can be explained by the fact that the densely packed rows of the adsorbate tend to be aligned along the densely packed rows in the substrate surface plane.

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